Arsenic Evaluation

There are several factors that are important to consider in the evaluation of the groundwater analytical results for arsenic generated at the Site to date.

- Potential analytical interferences;

- Total versus dissolved arsenic concentrations, including redox influences on arsenic concentrations;

- Regional background arsenic in soils; and

- Distribution of arsenic in groundwater.

The above factors contribute to the potential risks to the hypothetical future resident likely being overestimated. The Site-Related Groundwater Remedial Investigation (RI) Report (Arcadis, 2015) reported on the potential interference in arsenic analytical results from rare earth elements (REEs) as well as the contribution of particulates to the reported total arsenic concentrations. In addition, mild to moderate reducing conditions exhibited by groundwater in the PMP and OCDA are more favorable to arsenic solubility in groundwater, and the arsenic could be the result of natural or anthropogenic sources. Each of these evaluation factors are discussed in more detail in the following sections.

Potential Analytical Interferences

To demonstrate the potential analytical interferences, the analytical results for a select group of overburden and bedrock monitoring wells for arsenic using USEPA Method 6010 (subject to interference) were compared to the analytical results for arsenic using USEPA Method 7062 (a gaseous hydride atomic adsorption method not subject to this interference). As explained in the Site-Related Groundwater RI Report, the data from this analytical method comparison indicate the following:

- During the majority of the RI sampling activities, groundwater samples were analyzed for total and dissolved arsenic using Method 6010. As part of the Supplemental RI conducted in 2012, a supplemental evaluation was conducted using Method 7062 for arsenic analysis in order to compare the results.

- USEPA Method 7062 is the more sensitive analytical method and, consistent with this fact, the total arsenic results using this method are higher than the results generated during the bulk of the RI using USEPA Method 6010.

- Conversely, the dissolved arsenic results using USEPA Method 6010 are consistently higher than the dissolved arsenic results using USEPA Method 7062, indicating that the dissolved arsenic concentrations reported during the RI are biased high.

- As further discussed below, there is a correlation between the presence of particulates containing arsenic that are digested in the analytical process and higher total arsenic concentrations with large differences in total versus dissolved arsenic reported in groundwater samples from overburden monitoring wells.

- Conversely, total and dissolved arsenic concentrations are more similar for samples

collected from bedrock wells, which is as expected given that total arsenic levels will be lower given the lesser contribution from particulates containing arsenic.

Total versus Dissolved Arsenic Concentrations: Effects of Redox Conditions and Particulates

Under reducing conditions, the more soluble form of arsenic, As (III) or arsenite, will be the dominant species whereas, in more oxidized conditions, arsenic will occur as As(V) or arsenate, which tends to co-precipitate with other inorganics such as ferric iron and manganese IV and will largely be filtered out. As shown in the following table, the measured oxidation-reduction potential (ORP) at each of the well locations where arsenic is reported exhibits mild to moderately reducing conditions and, in the bedrock wells where particulates are less abundant, most of the total arsenic occurs in dissolved form.

Well	Arsenic Concentration, ug/L		ORP, mV
	Total	Dissolved	
Overburden Wells			
OB-11R	23.8	ND	-81
OB-16	7.9	0.78J	-66
OB-27	22.5	ND	-78
OB-31	12.8	ND	-76
OB-32	15.2	ND	-103
Bedrock Wells			
RW-2	4.3	4.8	-79
RW-3DD	16.8	16.6	-112
RW-3DS	14.7	13.5	-124
RW-5	8	7.9	-89
RW-10	6.6	7.2	-37
RW-12	13.5	15	-83
RW-14D	8.8	1.1	-140
RW-14S	14	11.3	-57
RW-15D	2.2	1.2	-95
RW-15S	12.7	7.8	-41

To illustrate the influence of sample particulates on arsenic concentrations in groundwater consider, as an example, the full data set from the August 2016 site-wide annual sampling event. For the 2016 sampling event, a total of 23 overburden wells and 48 bedrock wells were sampled. Of this total number of wells sampled, there were a total of 5 overburden wells and 10 bedrock wells in which either total or dissolved arsenic was detected in the groundwater sample. The 2016 data are summarized in the preceding table. The above data illustrate the effects of particulates on the reported arsenic results in groundwater at the overburden well locations in that there is a substantial difference between the results for total and dissolved arsenic at each of the overburden wells. Particulates are generally more likely to be present in the overburden wells than in a bedrock well because of the nature of the unconsolidated sediments in the overburden aquifer (e.g., fine-grained particulates can get through the filter pack). These results help to illustrate the comparability of total and dissolved results for the bedrock wells where sample particulates are less of a consideration and groundwater redox conditions have more of

an influence.

The State of New Jersey has classified the aquifers at the Site as Class IIA, meaning that groundwater can potentially be utilized for potable purposes. Therefore, the risk characterization would generally assume that a hypothetical future resident could be exposed to arsenic in groundwater via ingestion as drinking water as well as via inhalation and dermal contact while showering or bathing because, although groundwater is not used for potable or domestic purposes, the potential future use of groundwater is not currently prohibited based on the Class IIA classification of the aquifer. If groundwater is used for potable purposes, then a well would be subject to continual use. Under such circumstances, typically wells become fully developed, and particulates that initially may be present dissipate over time, and potentially re-occur for a short period of time if there is a disturbance to the system (e.g., a pump replacement, well rehabilitation). In addition, groundwater may be exposed to oxygen through pumping and aeration of the well in that process and co-precipitation of arsenic with iron, manganese and other inorganics may occur.

As noted above, the bias high in the reported arsenic concentrations due to particulates is evident in the overburden wells but not in the bedrock wells. While the shallow overburden aquifer is also designated Class IIA, it is much less likely to be used for potable purposes, in part because in the State of New Jersey, regulations at NJAC 7:9D-2.3(a)3i require a minimum of 50 feet of casing prior to the screened interval or open rock hole for a water supply well. Collectively, this information indicates that use of total arsenic concentrations from overburden wells has the potential to over-estimate risk, whereas there is not a material difference in the data for total and dissolved concentrations of arsenic in bedrock groundwater data. Dissolved arsenic data, therefore, are likely to be more representative of potential risk than total arsenic data.

Regional Background Arsenic in Soils

NJDEP has not established a regional background arsenic level in groundwater. However, that level has been implied in the regional background level of arsenic in soil. NJDEP's regional background arsenic level in soils is 19 mg/kg, as reflected in the Soil Remediation Standards at NJAC 7:26D. Because the risk-based soil remediation standards would be lower than this background level, the cleanup levels default to the background concentration, and this includes the default, Impact to Groundwater Soil Remediation Standard (IGWSRS), which is also set at 19 mg/kg.

The NJDEP guidance document entitled Development of Impact to Ground Water Soil Remediation Standards Using the Soil-Water Partition Equation (NJDEP, 2013) defines the calculation for inorganic IGWSRS as follows:

$$IGWSRS = C_{gw}\{(K_d) +(\theta_w + \theta_a H')/\rho_b\}DAF$$

Where:

C_{gw} = groundwater concentration, mg/L

K_d = soil water partition coefficient, L/kg

θ_w = water-filled porosity, dimensionless

θ_a = air-filled porosity, dimensionless

H' = Henry's law constant, dimensionless

ρ_b = dry soil bulk density, kg/L

DAF = dilution-attenuation factor

Arsenic is non-volatile, so the Henry's law constant is set to zero. The remaining default parameters established by the NJDEP along with the K_d for arsenic as inputs to this equation are as follows:

K_d = 26 L/kg

θ_w = 0.23

θ_a = 0.18

ρ_b = 1.5 kg/L

DAF = 20

Using these input parameters and setting the IGWSRS to 19 mg/kg, the resultant estimated groundwater concentration from soil-water partitioning is 36 ug/L. This is informative to the evaluation of arsenic because, for the complete dataset of arsenic concentrations in groundwater from 2008 to 2016 as used in this risk assessment, the following are total arsenic concentration statistics:

Minimum concentration – 0.57 ug/L

Maximum concentration – 36.1 ug/L

Arithmetic mean concentration – 2.8 ug/L

95% UCL concentration – 3.6 ug/L

What these data show is that, given the estimated groundwater concentration from soil-water partitioning is 36 ug/L and the maximum concentration reported in groundwater during the RI is 36.1 ug/L, the arsenic in groundwater could be explained solely by the natural presence of arsenic in soils. This is not to say that there could not be both natural and anthropogenic contributions to arsenic in groundwater. Rather, it does help to illustrate the absence of a defined anthropogenic source or groundwater plume.

Distribution of Arsenic in Groundwater

Figure X illustrates the 2016 distribution of arsenic concentrations in bedrock groundwater, in the area around the PMP and down gradient, both above and below the New Jersey GWQS. As shown, the occurrence of total and dissolved arsenic in groundwater at the Site is sporadic and temporal and, where it is reported, the distribution is not indicative of a plume. Rather, as discussed above, the results of the RI indicate that the reported concentrations of arsenic in groundwater are influenced by factors such as particulates in the samples which bias results high, redox conditions which often vary temporally, and contributions being as likely to be from regional, natural sources as they are from anthropogenic sources.

Conclusions

The foregoing analysis of the occurrence and distribution of arsenic in groundwater at the Site

leads to the following key conclusions:

- Arsenic in groundwater is as likely to be associated with the naturally occurring presence of this element as it is from an anthropogenic source.
- Because arsenic is also naturally occurring, the potential incremental risk calculated for this element is also associated with this natural occurrence and this fact should be considered in risk management decisions.
- Total arsenic concentrations in groundwater likely overestimate exposure point concentrations, particularly for the overburden groundwater.
- Risk characterization based on dissolved arsenic concentrations in groundwater is more likely to be representative of the potential incremental risk associated with this element.

Based on the information provided above, a sensitivity analysis of potential risk to the hypothetical future resident was evaluated including dissolved metals concentrations, including for arsenic. The cumulative potential cancer risk for the hypothetical future resident RME scenario for the adult, older child (or youth), and young child using dissolved metal concentrations is 1×10^{-4}, which is at the upper limit of USEPA's acceptable cancer risk range of 1×10^{-6} to 1×10^{-4}. As noted above, the dissolved metals concentrations in groundwater are considered more representative of the potential incremental risk, however, the potential incremental risk based on total arsenic concentrations is also be provided in the sensitivity analysis.